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1 Introduction Vacuum ultraviolet (VUV) spectroscopy of rare earth (RE) ions doped into wide band crystals has recently attracted considerable research interest due to numerous applica-tions for materials with optical activity in the VUV. Researches on the VUV spectroscopy are focused on understanding the level structure and relaxation mechanisms from high-energy localized states formed by mixed $4f^{n-1}5d$ configurations predominantly. The known peculiarity of the states involving 5d levels is high sensitivity to the crystal surrounding: their energy positions may change substantially from compound to compound [1]. Another major problem of spectroscopy of RE doped crystals consists in research of energy transfer processes of host electronic excitations to impurity centres [2, 3]. From this point of view we carried out an experimental study in VUV range for Sm^{3+} ($4f^5$), Tb^{3+} ($4f^8$), Er^{3+} ($4f^{11}$) and Tm^{3+} ($4f^{12}$) ions in SrF_2 crystals. In spite of the fact that SrF_2:RE^{3+} crystals are sufficiently studied systems in the past special attention to their VUV spectroscopy properties has not been paid.

The 5d levels of RE^{3+} ions doped into fluorite crystals are split by cubic O_h crystal field into low-energy doublet ^2E- and high-energy triplet $^2T_2$-subconfigurations. The interconfigurational $4f^n \rightarrow 4f^{n-1}5d$ transitions are more likely to the lowest tetragonal ^2E-component (x^2-y^2-orbital) and to the states of $^2T_2$-subconfigurations (xy-, xz-, and yz-orbitals) [4]. An excellent overview and analysis of $4f^n \rightarrow 4f^{n-1}5d$ excitation spectra for all RE^{3+} ions in YPO_4, CaF_2 and $LiYF_4$ has been presented in [5–7].

Our recent studies of VUV emission and $4f^n \rightarrow 4f^{n-1}5d$ excitation spectra of RE^{3+} ions doped into SrF_2 have been shown in [8–10]. A continuation of these studies as well as new results and discussions concerning peculiarities of excitation mechanisms for intra- ($4f^n \rightarrow 4f^n$) and interconfigurational ($4f^{n-1}5d \rightarrow 4f^n$) radiative transitions have been presented in this paper.

2 Experimental details The investigations were performed at the SUPERLUMI station (DESY, Hamburg). For excitation in 50-270 nm range a 2 m McPherson monochromator with a resolution of 3.2 Å was used. In VUV the spectral selection for excitation spectra measurements was performed with a 0.5 m Pouey-type monochromator (with a resolution of 10 Å) equipped with a photomultiplier R6836 (Hamamatsu). For detection of visible luminescence an ARC Spectra Pro-308i spectrograph equipped with a photomultiplier R6358P was used. The experiments were carried out at 8 K and 295 K.

SrF_2 crystals were grown in graphite crucible in fluorine atmosphere by the Stockbarger technique.

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3 Results and discussions

3.1 Intra-centre excitations Excitation spectra for $4f^n \rightarrow 4f^n$ emission of Sm^{3+} and Tb^{3+} in SrF_2 crystals are shown in Fig. 1 and Fig. 2, respectively. Structure of these spectra is predominantly determined by parity-allowed $4f^n \rightarrow 4f^{n-1}5d$ transitions to the different components of $4f^{n-1}5d$ configuration. The beginning of transitions to the lowest ^2E component is presented as a sharp increasing of the spectra at 168 nm for Sm^{3+} and 210 nm for Tb^{3+} ions.

In the case of Sm^{3+} ions additional bands are caused by Coulomb interactions of lowest ^2E state with various multiplets of residual $4f^4$ core of excited $4f^45d$ configuration [7]. The $4f^4$ core corresponds to nonexcited Pm^{3+} ions which has a dense enough levels set in wide energy range. Therefore it is possible to conclude that additional bands make contribution to intensity of the spectra up to fundamental absorption edge of SrF_2 at 119-121 nm [9]. Since crystal field splitting of 5d orbital in SrF_2 is about 19800 cm^{-1} (2.45 eV) [11] it is possible to assume that transitions to the states of high-energy $^2T_2$ subconfiguration are observed at 121-127 nm. A nature of low intense bands at 170-186 nm will be discussed below.

The $4f^75d$ states of Tb^{3+} spectra are particularly accessible to analysis because the energy difference between the lowest states of $4f^7$ core and the next-lowest states is about 30000 cm^{-1} (3.72 eV), larger than crystal field splitting of 5d orbital. So the transitions to the lowest ^2E states of $4f^75d$ configuration are observed as intense bands at 210 nm and at 120-140 nm. In accordance with crystal field splitting of 5d orbital the transitions to the high-energy triplet $^2T_2$ sets are presented in the spectra as broad bands at 145-172 nm. A group of bands observed at 168-200 nm are mainly caused by excitation of RE^{3+} centers situating in cluster formations, which are more probable at concentration increasing. Moreover, we assume that 183.5 nm band can be connected with f-d transitions to the second tetragonal ^2E component.

Tb^{3+} ions belong to subgroup of "heavy" lanthanides for which spin-forbidden transitions to high-spin (HS) states are possible [6]. In the spectra of SrF_2:Tb^{3+} such transitions are observed at 255 nm.

Excitation spectra of Er^{3+} and Tm^{3+} ions are presented in Fig. 3 and Fig. 4, respectively. For both ions the structure of $4f^{n-1}5d$ configuration is clearly observed in the spectra recorded monitoring $4f^{n-1}5d \rightarrow 4f^n$ emission. The detailed analysis of these spectra can be found elsewhere [10]. As is shown in the figures the spectra recorded for $4f^n \rightarrow 4f^n$ emission demonstrate opposite behaviour to those for $4f^{n-1}5d \rightarrow 4f^n$ emission. It reflects partly the variation of absorption coefficient in the transparency range and the competition in the energy transfer processes to the $4f^{n-1}5d$ and $4f^n$ emitting levels.

In [12, 13] it was shown that fluorite synthetic crystals demonstrate intense enough optical absorption in 130-200 nm spectral range that is connected with presence of uncontrolled oxygen impurities which are falling into crystals from crucible and residual atmosphere at growing using Stockbarger method. We assume that such oxygen centres (oxygen-vacancy defects and their aggregates) make appreciable contribution to excitation of $4f^n$ levels. As a rule, the absorption of oxygen centres is observed as very

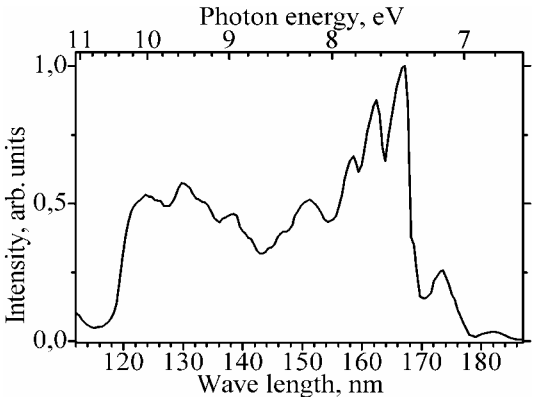

Fig. 1 Excitation spectrum for $^4G_{5/2} \rightarrow {}^6H_{7/2}$ emission at 598 nm of Sm^{3+} ions in SrF_2:0.1%Sm^{3+}. T = 8 K.

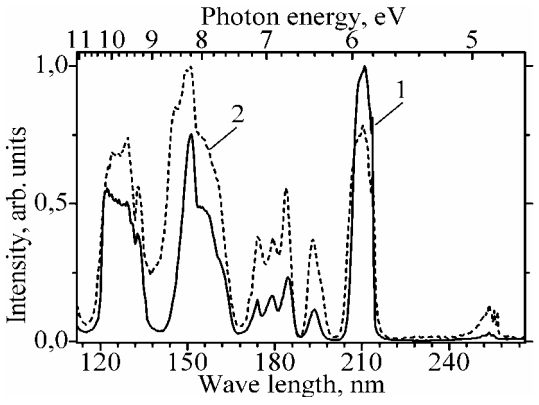

Fig. 2 Excitation spectra for $^5D_3 \rightarrow {}^7F_6$ emission at 385 nm of Tb^{3+} ions in SrF_2:0.05%Tb^{3+} (1) and SrF_2:1%Tb^{3+} (2). T = 8 K.

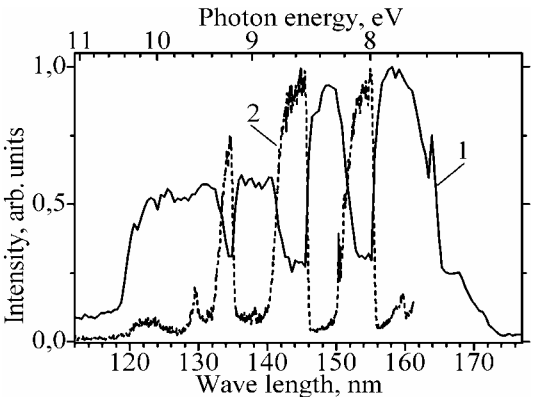

Fig. 3 Excitation spectra for $^4S_{3/2} \rightarrow {}^4I_{15/2}$ emission at 550 nm (1) and for $4f^{10}5d(HS) \rightarrow {}^4I_{15/2}$ emission at 165 nm (2) of Er^{3+} ions in SrF_2:0.1%Er^{3+}. T = 8 K.

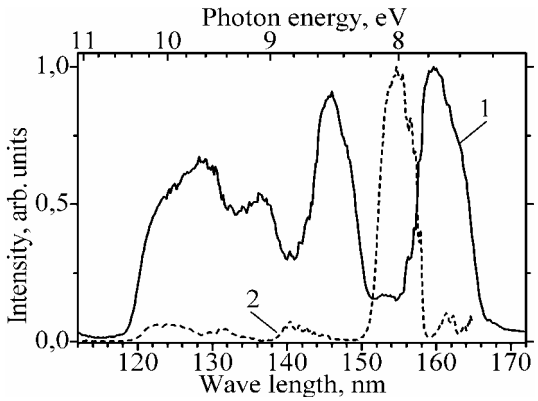

Fig. 4 Excitation spectra for $^1G_4 \rightarrow {}^3H_6$ emission at 451 nm (1) and for $4f^{11}5d(HS) \rightarrow {}^3H_6$ emission at 167 nm (2) of Tm^{3+} in SrF_2:0.3%Tm^{3+}. T = 8 K.

broad and intense bands in excitation spectra. In the case of RE^{3+} doped crystals these absorption processes compete with intense absorption bands caused by $4f^n \rightarrow 4f^{n-1}5d$ transitions. It results in observing atypical peculiarities of excitation spectra for $4f^n \rightarrow 4f^n$ emissions. The atypical peculiarities are strongly pronounced for ions having radiative $4f^{n-1}5d$ states (such as Er^{3+} and Tm^{3+}). In these ions a dominating way of relaxation of excited $4f^{n-1}5d$ states is VUV emission [6, 10].

For RE^{3+} ions having no $4f^{n-1}5d \rightarrow 4f^n$ emission the energy of excited $4f^{n-1}5d$ states is transferred with high efficiency to the $4f^n$ levels. In this case such incidental processes as absorption connected with oxygen impurity cannot compete with intensity of excitation through direct $4f^n \rightarrow 4f^{n-1}5d$ transitions. In excitation spectra of such ions the bands of oxygen absorption are either weakly observed (as in the case of Sm^{3+}) or completely unobserved (case of Tb^{3+}).

A common property for crystals doped with Er^{3+} or Tm^{3+} is high intensity of $4f^n \rightarrow 4f^n$ emission upon excitation in the range of long-wavelength fundamental absorption edge of the host. For $4f^{n-1}5d \rightarrow 4f^n$ radiative transitions in contrary such mechanism is suppressed. This phenomenon can be caused by so-called autoionization state [2] that is a result of promotion of one electron to high-energy excited 5d-states located in conduction band at absorption. Finally, an exciton-like $Ln^{4+} + e^-$ (bounded) formation is created that relaxes predominantly into the 4*f* manifold through dipole-dipole or multipole interactions.

3.2 Band-to-band excitations For determining the main energy transfer mechanisms from host electronic excitations to impurity centres the measurements were extended up to the fundamental absorption range of the host. The excitation spectra for $4f^n \rightarrow 4f^n$ emission of Tb^{3+} and $4f^{n-1}5d \rightarrow 4f^n$ emission of Er^{3+} are shown in the Fig. 5 and Fig. 6, respectively.

As evident from the figures, the intra- and interconfigurational emission of RE^{3+} is efficiently excited in the energy range of direct optical formation of excitons in SrF_2 both at 8 K and at 295 K. An electron-hole mechanism of impurity excitation is well observed in the excitation spectra for $4f^n \rightarrow 4f^n$ emission of Tb^{3+}. At temperature of 8 K it is needed to expect a high extent of freezing of hopping diffusion of self-trapped holes and as well a small mean free path of hot holes before their self-trapping. In spite of this fact we observe a relatively effective excitation process of $4f^n \rightarrow 4f^n$ emission (taking into account reflection and near-surface losses).

Fig. 6 shows considerable fact that irrespective of temperature the high-energy $4f^{n-1}5d \rightarrow 4f^n$ emission of Er^{3+} is practically not excited at the energies from the edge of band-to-band transitions up to some threshold energy of 19 eV after which a sharp increasing of emission is observed. It is obvious that observed threshold cannot be result from beginning of photon multiplication.

In [14] it was shown that in wide band crystals an effective mass of photoelectron is significantly smaller than that of a hole that results in the photoelectrons gain the main part of the photon energy on

the band-to-band excitation. In our opinion just the hot conduction photoelectrons play the key role in impurity excitation processes in $SrF_2:RE^{3+}$ crystals. The main distinction in excitation of $4f^n \rightarrow 4f^n$ and $4f^{n-1}5d \rightarrow 4f^n$ emission consists in threshold of energy at which the direct impact excitation by hot photoelectrons starts to be possible. So, in the case of interconfigurational emission of Er^{3+} the hot photoelectron must possess energy sufficient to excitation of high-energy localized 5d states ($E_{f\text{-}d} > 7.75$ eV [8-10]). For intraconfigurational emission, on the contrary, it is not so critical because $4f^n$-configuration is characterized by large set of closed localized levels in wide energy range.

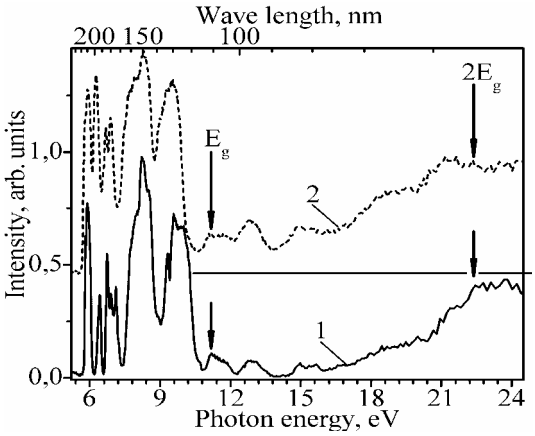

Fig. 5 Excitation spectra for $^5D_3 \rightarrow {}^7F_6$ emission at 385 nm of Tb^{3+} ions in SrF_2:1%Tb^{3+} at T = 8 K (1) and T = 295 K (2).

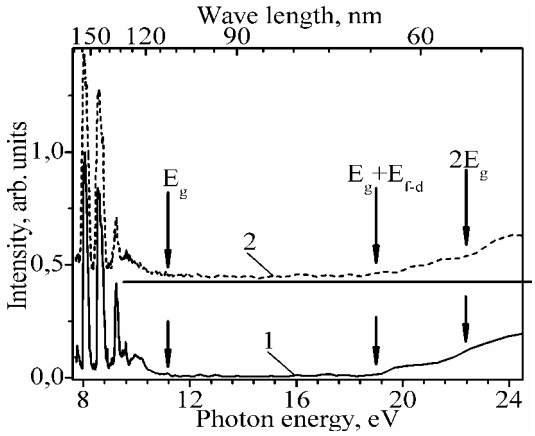

Fig. 6 Excitation spectra for $4f^{10}5d(HS) \rightarrow {}^4I_{15/2}$ emission at 165 nm of Er^{3+} ions in SrF_2:0.1%Er^{3+} at T = 8 K (1) and T = 295 K (2).

4 Conclusion There are several essential distinctions of excitation mechanisms for intra- and interconfigurational radiative transitions in RE^{3+} ions in SrF_2. At intra-centre excitation the $4f^{n-1}5d \rightarrow 4f^n$ emission can be excited only through direct populating of $4f^{n-1}5d$ states while $4f^n \rightarrow 4f^n$ emission can be efficiently excited not only through populating of $4f^n$ or $4f^{n-1}5d$ states but also through relaxation of excited states connected with uncontrolled growth impurities and autoionization of RE^{3+} ions. Under band-to-band excitation the energy transfer from host electronic excitations to impurity is realized through relaxed excitons and direct impact excitation by hot conduction photoelectrons.

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